UDC 666.1.022.2:666.127:621.926.4.002.237

THE EFFECT OF CULLET GRINDING IN IMPACT-REPULSION MILLS ON THE PROPERTIES OF GLASS POWDERS

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The change in the structural and energy properties of the glass powders resulting from rapid grinding of the cullet in an impact-repulsion mill is considered. The increase in crystallization capacity of the glass powders attributed to this effect is discussed. This effect must be taken into account in production of the foam glass, filters, membranes, and partitions.

Glass powders with fraction size below 0.08 μm are used in the production of foam glass, glass filters, porous sorbents, porous partitions, and other materials.

The traditional method of cullet grinding in order to obtain powders consists in dispersion of glass in a dry-grinding ball mill lined inside with silicon plates, where the milling bodies in the form of silicon pebble, uralite balls, or cylinders (cilpebs) act upon the initial glass fragments. The impact and attrition in this case are the main types of cullet deformation in grinding. This method makes it possible to obtain glass powders of white color without impurities, but the milling lasts a considerable time, and the amount of screened particles requiring additional milling is significant.

In recent years different branches of industry have been introducing mills based on the impact-repulsion action (IR). This mill (Fig. 1) consist of a cylindrical case made of St.45 steel, and inside the case there is a rotor with beaters made of St.3 steel. The rotor with beaters is driven by a synchronous motor through a system of transmissions, which makes it possible to vary the rotational speed of the rotor over a wide range (from 6000 to 12 000 min^{-1}). Glass cullet whose fragments are up to 15 mm in size is fed into the charge opening and then subjected to multiple action of the beaters inside the mill. The glass pieces flying at a high speed toward the case walls undergo strong impacts and are repelled from the case wall and subjected to new impacts of the beaters, and this cycle is multiply repeated. The duration of a single contact of a glass fragment with the beaters of the mill case is estimated at 10^{-4} sec. The total time the cullet stays in the mill (from loading to discharge) is 1 – 1.5 sec.

The multiple powerful blows against the beaters and the mill case soon destroy the glass fragments. The obtained glass powder arrives through a discharge opening into a cy-

clone where it settles and passes to a receiving bag, while the air is removed through a pipe to a bag filter where it is completely purified from dust. The effect of the glass particles (5.5 – 6 on the Mohs hardness scale) on the beaters and the mill case results in the contamination of the glass with metals; therefore, the glass powder acquires a gray color. However, the milling intensity in this case increases many times over.

The present paper describes the results of studying the effect of the milling conditions in the IR mills on the properties of glass powders, including their behavior in heating. For comparison, reference milling of glass cullet was performed in a laboratory ball mill. The weight of the milled material in all cases was 1.5 kg. The grinding lasted 5 h in the ball mill and 20 min in the IR mill.
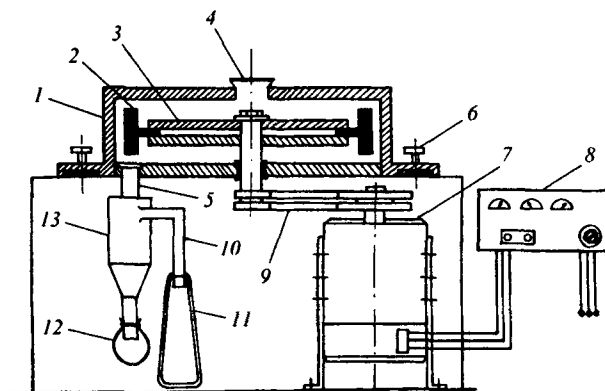

Fig. 1. Diagram of an impact-repulsion mill: *1*) mill case; *2*) working beaters; *3*) rotor; *4*) charge opening; *5*) case sealing; *6*) cap screw; *7*) synchronous motor; *8*) control panel; *9*) rotor drive; *10*) air discharge pipe; *11*) bag filter for air purification; *12*) receiving bag; *13*) cyclone.

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The grinding in the IR mill was performed at a rotor speed of 8000, 9500, and 10,000 min^{-1}. All powders in this case had a gray color of varying intensity. Using the sulfosalicylate method [1], the quantity of milled metal in the glass powders was determined. Thus, the weight content of Fe for the above described milling conditions was (%): 0.22, 0.25, and 0.39 (converted to Fe_2O_3 it is 0.30, 0.35, and 0.56, respectively). This is evidence of the increasing abrasive effect of the cullet on the structural parts of the IR mill as the rotational speed of the rotor increases.

The fractional composition of the glass powders was determined by sifting them through a set of sieves: Nos. 025, 0.18, 0125, 008, 0063, and 0056. The fractions which passed through a No. 0056 sieve were subjected to sedimentation analysis using the pipette method [2]. The granulometric compositions of the glass powders are listed in Table 1.

As can be seen, the milling of cullet in a IR mill not only is more intense compared to a ball mill, but leads to a higher yield of fine fractions (< 56 μm). The amount of these fractions for a ball mill is 14%, while for the IR mill the residue on a No. 025 in the first case is ~77%, and in the second case it is 10 – 17%.

After grinding in a ball mill, all of the unmilled glass particles to a great extent retained their laminar shape but had dulled edges and lusterless surface. This supports the assumption that the shear deformation (attrition) of glass fragments is quite typical of the ball mill, along with the impact deformation.

The shape of the glass powder particles after milling in the IR mill is more isometric, which shows that the impact deformation plays the leading role in this type of mill. The powerful impacts of the rotor beaters and the mill case on the pieces of cullet inside the mill produce intense shock waves which pass through the glass particles within a short time (10^{-4} sec per each contact) and cause numerous microcracks in various directions. The equation of movement of the destruction front into the depth of glass has the following form [3]:

$$\frac{dx}{d\tau} = \frac{\sigma_{max}^n}{\partial / \partial x \left(\int_0^{\tau} \sigma_{max}^n d\tau \right)},$$

where x is the coordinate with respect to the glass surface (the crack depth); τ is the current time; σ_{max} is the maximum tensile (impact) stress arising in the glass under the effect of the grinder.

It is obvious that σ_{max} and x increase with increase in the speed of the rotor. The microcracks expanding and overlapping each other gradually bring about brittle disintegration of the initial glass pieces into smaller fragments. At the same time, the powerful shock waves passing through the glass particles, which remain undestroyed although their size keeps decreasing, at some moment causes many of

Si – O – Si bonds to break and switch over to the neighbors (similarly to high-viscosity flow according to R. L. Muller [4]). In this case, the angle of the Si – O – Si bond can vary within certain limits, which points to the "pumping" of part of mechanical energy into the glass, the transition of mechanical energy into internal energy, and an increase in the surface component of the glass enthalpy. Moreover, the same powerful shock waves passing via the structural lattice of glass on switching over of the Si – O – Si bonds, facilitate the emergence of microprotrusions on the surface of the glass particles (similar to the outcrop of dislocations on the surface of crystal bodies), which increases as well the surface component of glass enthalpy. Consequently, a more pronounced change in the glass structure can be expected if the glass is milled in an IR mill rather than in a ball mill. The experimental data confirm this assumption.

The diffraction pattern (DRON-2, CuK_α-radiation) of the glass powder obtained in the ball mill does not show any noticeable reflections in the entire spectrum of slide angles, from 8 to 70° (Fig. 2). The diffraction patterns of the powders obtained in the IR mill exhibit relatively low peaks in the region of the angles of 19 – 27, 31 – 33, 44 – 45, and 60 – 61°, and when the rotor speed is 10,000 min^{-1}, these reflections become more perceptible. It is significant that the peaks are nor sharp but have a "diffuse" shape. This is evidence of the high degree of defectiveness arising in milling of the ordered areas in the glass structure. Attempts to rely on these reflections, in order to uniquely identify the phases presumed to be of the type of α- and β-quartz, β- and α-crystobalite, and devitrivite, using the dependence tables $d/n = f(2\theta)$ and the ASTM database were not successful. In our opinion, the reason for this lack of clarity is as follows.

As was earlier mentioned, a single contact of a glass particle with the parts of the IR mill lasts 10^{-4} sec, and the total duration of the cullet batch passing through the mill is 1 – 1.5 sec. This time is only sufficient for intense destruc-

TABLE 1

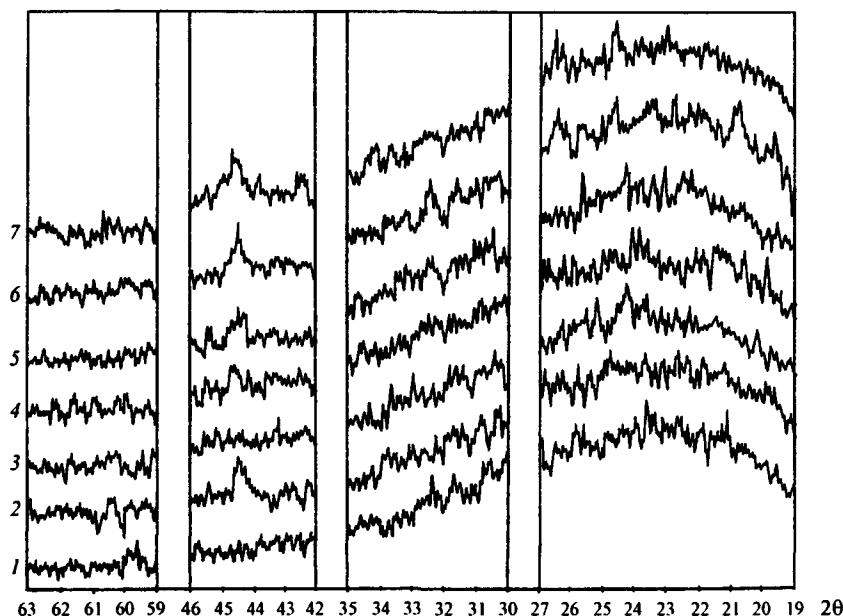| Particle size, μm	Granulometric composition (%) of glass powders milled			
	in ball mill	in IR mill with a rotor speed of, min^{-1}		
		8000	9500	10,000
> 250	76.92	10.84	17.10	9.49
180 – 250	1.02	5.46	7.02	4.50
125 – 180	2.10	14.46	15.15	10.33
80 – 125	2.24	20.51	16.87	13.51
63 – 80	2.36	5.54	3.81	6.35
56 – 63	1.53	12.30	8.87	8.96
10 – 56	7.35	13.16	12.07	21.34
5 – 10	3.50	13.30	11.27	18.98
1 – 5	2.20	3.86	5.90	3.16
< 1	0.78	0.60	1.99	2.39

Fig. 2. Diffraction patterns of glass powders obtained in a ball mill (*1*) and an IR mill after milling (*2, 4, 6*) and after 10 days of storage in air (*3, 5, 7*) with a rotor speed of 8,000 (*2, 3*), 9,500 (*4, 5*) and 10,000 min^{-1} (*6, 7*).

tion of the glass structure and supply of excessive energy, and more or less definite conditions for the appearance of nucleation and prenucleation crystal centers develop only on the surface of the glass particles. Apparently, these nucleation centers have a two-dimensional nature (since their growth on the surface has two degrees of freedom) and not a three-dimensional habitus.

The usual thermal crystallization of glass at a temperature above t_g and with viscosity below 10^{12} Pa · sec lasts tens of seconds, sometimes several hours, which allows the crystals to form as three-dimensional bodies. The two-dimensional nuclei (the surface "crystals") have a deformed structure and are metastable. The interplanar distance tables in the ASTM database only contain the values of d/n for three-dimensional stable crystals. That is why it is difficult to attribute the reflections in the diffraction patterns of the glass powders (Fig. 2, diffraction patterns *2, 4*, and *6*)) to specific stable phases. An interesting fact was discovered to support this assumption: after 10 or more days of storage in air, some reflections in the powders obtained in the IR mill either weaken, or completely disappear (Fig. 2, diffraction pattern *7*).

Thus, the considered two-dimensional ordered surface formations are thermodynamically unstable, so the structure of the surface layers of glass particles relaxes with time, and the two-dimensional nucleation and prenucleation groups gradually disappear. Moreover, along with the disappearance of some peaks (19 – 22, 44 – 45, and 60 – 61°) some new reflections (24 – 25 and 32 – 34°) appear in the diffraction patterns. All this points to the complex structural (volume and

surface) state of the glass particles after grinding of cullet in a IR mill.

In this context, it is interesting to study the behavior of glass powders obtained in different milling conditions while being heated up to temperatures above t_g, when thermal crystallization starts in glass.

The freshly milled glass powders were put into corundum crucibles and placed in a muffle electric furnace, then heated up to temperatures of 580, 600, 610, and 610°C and held for 25, 35, and 45 min, after which the cakes were subjected to x-ray phase and electron microscopic analysis.

Figure 3 shows the diffraction patterns of the glass powders held in the furnace at a temperature of 580°C for 35 min. The diffraction patterns of the caked glass obtained in the ball mill differs insignificantly from the pattern of the reference glass (Fig. 2, diffraction pattern *1*). In the cakes of the powders obtained in the IR mill at a rotor speed of 8000 min^{-1}, the reflections inherent in two-dimensional metastable phases disappear and the new weak reflections arise in the region of angles 20 – 21°. The cakes of the glass obtained with a rotor speed of 9,500 and 10,000 min^{-1} clearly exhibit the β-quartz reflections (25.52, 37.92, and 68.05°). Thus, the glass powders obtained in the IR mills have an increased crystallizing capacity when heated, as compared to the powders obtained in the ball mills.

The electron microscopic studies support this conclusion. Figure 4 shows photos of platinum-carbon replicas of the glass cakes after firing at a temperature of 620°C for 45 min. The photos of the glass powder cakes obtained in the IR mill with a rotor speed of 8000 min^{-1} do not exhibit any perceptible indications of thermal crystallization, and with a rotor speed of 9500 and 10,000 min^{-1} the formation of crystals and the development of cracks caused by shrinkage between them are clearly visible.

The cellular texture observed in crystallization products of the glass powders obtained in the IR mill can be related to the outcrop on the glass particle surface of dislocation steps caused by the movement of impact waves over the bulk of the glass structural lattice, and the incorporation of metallic iron microparticles, which at a temperature of 580 – 620°C oxidize to an oxide (Fe_2O_3) acting as a crystallization initiator, into the surface layers of glass.

Let us summarize the physicochemical background of the experimental results.

It is known that glass is characterized by excess enthalpy ΔH_{gl}, as compared to a compound of the same composition in a crystalline state (Fig. 5). Obviously, within the temperature range of 298 K – (t + 273) K, where 298 K is room tem-
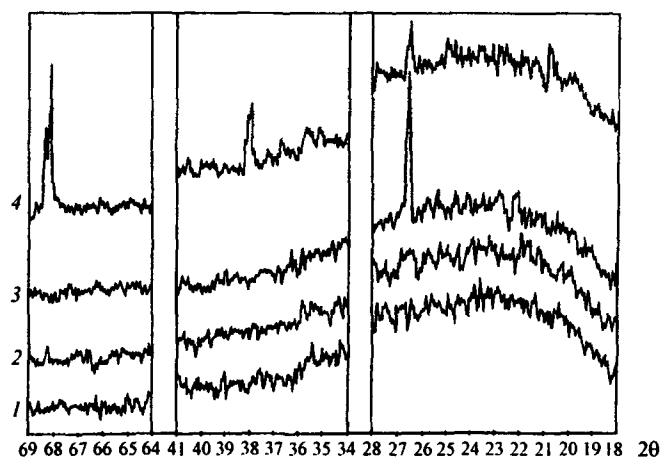
69 68 67 66 65 64 41 40 39 38 37 36 35 34 28 27 26 25 24 23 22 21 20 19 18 2θ

Fig. 3. Diffraction patterns of cakes of glass powders (sintering temperature 580°C) obtained in a ball mill (*1*) and in an IR mill (*2, 3*, and *4*) at a rotor speed of 8,000, 9,500, and 10,000 min⁻¹, respectively.

perature and $(t + 273)$ is a temperature above t_g, the glass enthalpy will have the following form:

$$H_{gl} = H_{gl}^0 + \int_{298}^{t+273} C_{p_{gl}} \, dT \,,$$

and the enthalpy of crystals, accordingly:

$$H_{cr} = H_{cr}^0 + \int_{298}^{t+273} C_{p_{cr}} \, dT \,,$$

where H_{gl}^0 and H_{cr}^0 are the enthalpy of glass and crystals (respectively) in the initial state; $C_{p_{gl}}$ and $C_{p_{cr}}$ are the heat capacity of glass and crystals, respectively.

For point *2* in Fig. 5 (after the melting of the crystal is completed) the following equality is true:

$$H_{gl}^0 + \int_{298}^{t+273} C_{p_{gl}} \, dT = H_{cr}^0 + \int_{298}^{t+273} C_{p_{cr}} \, dT + \Delta H_m \,,$$

from whence

$$\Delta H_{gl}^0 = H_{gl}^0 - H_{cr}^0 = \Delta H_m + \int_{298}^{t+273} (C_{p_{cr}} - C_{p_{gl}}) dT$$

or

$$\Delta H_{gl}^0 \approx \Delta H_m \approx -\Delta H_{cr} \,,$$

i.e., the excess enthalpy of glass H_{gl}^0 compared to the enthalpy of crystals is approximately equal to the thermal ef-

Fig. 4. Electron microscopic photos (×5000) of glass powder cakes (sintering temperature 620°C): *a, b*, and *c*) rotational speed of the rotor of 8,000, 9,500, and 10,000 min⁻¹, respectively.

fect of crystal melting ΔH_m or the heat of glass crystallization taken with the reverse sign.

Line *1 – 2* in Fig. 5 characterizes the process of the melt vitrification.

In the milling of glass cullet in IR mills, the particles are "pumped," i.e., the enthalpy H_{ch} increases, and the more intense the milling conditions, the higher (in the general case, if no spontaneous crystallization occurs) the level of energy supplied to the glass. According to some authors, the excess
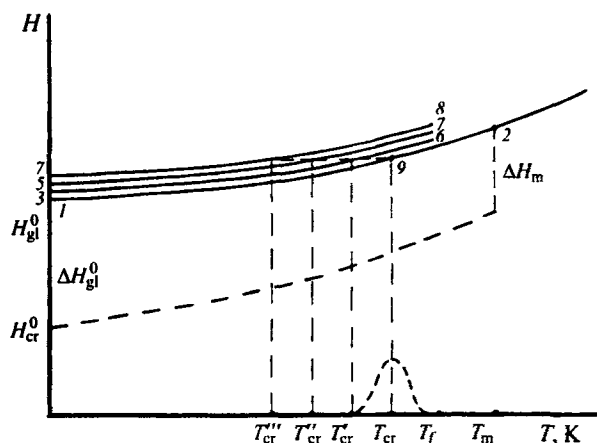
Fig. 5. Enthalpy of glass versus temperature.

of internal energy ΔH_{ch} accumulated by the solid body milled in a IR mill comprises 7 to 10% of the destruction energy supplied to the body. Then, the excess of enthalpy in the glass powders obtained in different milling conditions will be:

$$\Delta H'_{gl} = \Delta H^0_{gl} + \Delta H'_{ch};$$

$$\Delta H''_{gl} = \Delta H^0_{gl} + \Delta H''_{ch};$$

$$\Delta H'''_{gl} = \Delta H^0_{gl} + \Delta H'''_{ch},$$

whereas, $\Delta H'_{ch} < \Delta H''_{ch} < \Delta H'''_{ch}$.

The dependences of the type of $\Delta H'_{gl} = f(T)$ in Fig. 5 are represented by curves $3-4$, $5-6$, and $7-8$ (for a rotor speed of 8000, 9500, and 10,000 min^{-1}, respectively).

In order for the glass to crystallize in heating, it should be heated up to the temperature of formation of crystalliza-

tion centers T_{cr}, and activation energy should be supplied to the glass, equal to

$$E_A = \int_{298}^{t_{ep} + 273} (C_{p_{cr}} - C_{p_{gl}})\, dt.$$

If a horizontal line corresponding to the level E_A is passed from point 9, it will intersect the dependence of the type of $\Delta H'_{gl} = f(T)$ at different points. By dropping perpendiculars from these points to the abscissa axis, we find that at the attained level of E_A, the powders obtained in different milling conditions in the IR mill have lower crystallization temperatures $(T'''_{cr} < T''_{cr} < T'_{cr})$ than the glass powders obtained in the ball mill, which is quite obvious in the context of thermodynamics. The presence of the crystallization initiator (Fe_2O_3) in the system intensifies even more the tendency of the glass powders for conversion in heating to a more stable (crystalline) state.

Consequently, the grinding of glass cullet in the impact-repulsion mills in intense conditions (with a rotor speed of $9500 - 10,000\ \text{min}^{-1}$) contributes to an increase in the crystallizing capacity of glass powders, which ought to be taken into account in the production of foam glass, filters, membranes, partitions, etc.

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